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(54) Title: FUNGICIDAL COMPOSITION AND METHOD OF CONTROLLING FUNGUS INFESTATION

(57) Abstract

If the R-enantiomer of metalaxyl, furalaxyl or benalaxyl is used, this results in a markedly increased biodegradability of these plant fungicides in the soil and a higher activity on the plants, as compared with the data of the racemic active ingredients. Fungicidal compositions exhibiting said improved properties comprise either of these fungicides with a content of R-enantiomer of more than 70 per cent by weight based on the total amount of active ingredient.

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Fungicidal composition and method of controlling fungus infestation

The present invention relates to a novel method of controlling and preventing Oomycete infection of plants by using metalaxyl, furalaxyl or benalaxyl, hereinbelow termed active ingredient I, in each case with an R-enantiomer content of over 70 % by weight, and to suitable fungicidal compositions for this purpose.

Metalaxyl was the first commercially available preparation from the series of the class of active ingredients originally termed acylalanines, later phenylamides, which are outstandingly active against Oomycetes. The Oomycetes include all downy mildews, which attack mainly potatoes, tomatoes, vines, hops, maize, sugar beet, tobacco, vegetables, lettuce, but also bananas, rubber, as well as lawns and ornamentals.

The preferred application of the acylalanine fungicides is foliar application, the foliage and the growing plant being treated with the active ingredient. Some of the active ingredient is taken up by the plant, but some remains on the plant and is washed off by the rain or otherwise taken up by the soil due to leaf drop or time of maturation. In the case of soil application, the active ingredient is incorporated into the soil directly by applying it in liquid form, or, for example, by means of granules.

A disadvantage in this context is the slow degradation rate of the representatives of this substance class in the soil, which depends largely on whether the soils are humous soils, mixed sandy/loamy soils or strongly adsorptive soils (loam/clay). In the case of prolonged treatment periods, on the one hand in perennial crops, such as grapevines, on the other in typical soil crops, such as potatoes, sugar beet or lawns, the soils may be subjected to cumulative loading with acylalanine fungicides, which, in turn, are an environmental hazard, but in particular a groundwater hazard.

Metalaxyl is N-(2,6-dimethylphenyl)-N-(methoxyacetyl)-DL-alanine methyl ester.

Benalaxyl is N-(2,6-dimethylphenyl)-N-(phenylacetyl)-DL-alanine methyl ester.

Furalaxyl is N-(2,6-dimethylphenyl)-N-(2-furanylcarbonyl)-DL-alanine methyl ester.

The compounds are known from the literature. The degradation data given vary. The reference book "The Pesticide Manual", 10th Edition 1994, edited by the British Crop Protection Council, gives the following information on the hydrolytic half-lives of these products. (DT = disappearance time).

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Metalaxyl: DT-50 (20°C) pH1:>200 d

pH9:115 d

Benalaxyl: DT-50 pH9.25: 86 d

Furalaxyl: DT-50 (20°C) pH1:>200 d

pH9:>200 d

These data show an undesirably high stability in the aqueous medium.

Attempts were made to accelerate the degradation behaviour by means of suitable formulations, for example by means of hydrophobic additives which prevent deeper penetration of the active ingredient into the soil and expose it on the surface to the incidence of sunlight and to elevated temperatures. It was attempted to exploit a further disadvantageous property of the acylalanine fungicides, namely their high volatility, which is a nuisance under the effect of sun and high temperatures. It would have been expected that the volatility of the active ingredient on the soil surface would be equally high, a fact which has not been observed in practice.

All these attempts have not resulted in convincing solutions. Once the active ingredient is adsorbed by the soil surface, even only within the uppermost 2 cm, degradation is reduced drastically, which entails all the adverse consequences of sparingly degradable active ingredients which the expert is familiar with.

Entirely surprisingly, it has now been found that the solution of this problem is found in the acylalanine active ingredient itself, in which the R-enantiomer is, unexpectedly, degraded more rapidly than the S-enantiomer or than the commercially available active ingredients which are based on the racemates in question. Since 1975, which is when this substance class became known, one has been familiar with the fact that it is the R-enantiomer anyway which is the more fungicidally active ingredient (cf. e.g. GB-1 500 581).

As a solution for practical use, the literature has never seriously proposed, in 19 years, the allegedly adjacent solution of using, from the start, the respective R-enantiomer of an acylalanine fungicide. On the one hand, one must not underestimate the technological difficulties of preparing an R-enantiomer in pure form or an active substance enriched with R-enantiomer (for example fractional crystallization of the racemate or stereospecific synthesis), on the other hand there was no incentive and no technological necessity for the practitioner for acting in such a way. However, the decisive factor is this. It could not have

been assumed that a reduction or complete elimination of the proportion of S-enantiomer in the racemate would solve the problem of the unduly long residence time of the active ingredient in the soil. As yet, no R-enantiomers, or R-enantiomer-enriched racemates, of acylalanine fungicides have been put on the market. With respect to the overall ecological situation of the otherwise effective control of downy mildews (Oomycetes) with acylalanine fungicides, in particular with metalaxyl, the solution of the degradation problem proposed herein is of decisive technological importance in agricultural practice worldwide. It is a standard demand in crop protection to achieve an optimal effect with an active ingredient at the lowest dosage rate required while simultaneously keeping the pollution of the environment as low as possible.

In the field of the acylalanine fungicides, in particular in the case of its main representative, metalaxyl, this problem can be considered as solved. An evidently better biodegradability in the soil is achieved if the content of R-enantiomer in the active ingredient is over 70 % by weight.

The present invention provides an ecologically desirable method of controlling and preventing Oomycete infestation of plants by using an R-enantiomer of metalaxyl or benalaxyl

 $R = OCH_3$ (R-metalaxyl) $R = C_6H_5$ (R-benalaxyl) or by using the R-enantiomer of furalaxyl

$$CH_3$$

$$C - COOCH_3$$

$$CH_3$$

$$CO - COOCH_3$$

$$CH_3$$

$$CO - COOCH_3$$

$$CH_3$$

$$CO - COOCH_3$$

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in each case at least 70 per cent by weight of the particular amount of total active ingredient.

Here and below, the racemates of the three active ingredients metalaxyl, benalaxyl and furalaxyl are termed active ingredient I. With increasing contents of R-enantiomer in the active ingredient the degradation properties in the soil are improved.

The invention preferably relates to a method of controlling Oomycetes in which the active ingredient employed has an R-enantiomer content of over 85 % by weight, in particular over 92 %, and preferably over 97 %, based on the total amount of active ingredient. Particularly preferred is the method in which the active ingredient I is essentially composed of R-enantiomers and is essentially free of S-enantiomers (< 1 %).

The present invention furthermore relates to a composition for controlling Oomycetes in which the amount of R-enantiomers in active ingredient I amounts to over 70 % by weight, preferably 85 % by weight, and particularly prefered over 92 %, based on the total amount of active ingredient. In particular, the invention relates to a composition wherein the content of the R-enantiomer in the active ingredient is more than 97 % by weight and especially to one wherein the active ingredient is essentially free from S-enantiomer (< 1 % by weight). The indicated percentages do not take into account that technically produced active ingredient additionally contains traces of by-products and intermediates (ca. 3-5 % b.w.).

The composition and the method of the present invention control, amongst the Oomycetes, in particular fungal pests from the group of the Peronosporales, in particular Plasmopara viticola, furthermore Phytophthora spp., such as P. infestans, Pythium pathogens, Bremia, Pseudoperonospora and others.

The rates per application (spraying, dusting, incorporation into the soil and the like) are 60 g of active ingredient per hectare (a.i./ha) to 300g of a.i./ha based on the pure R-enantiomer.

The active ingredient employed can be furalaxyl, benalaxyl, but preferably metalaxyl. Formulations of R-metalaxyl are preferably highly concentrated (more than 30 % b.w. of active ingredient). This results in savings in transport and storage capacity.

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Furthermore, pathogens on live plants have revealed that the activity displayed by the R-enantiomer of active ingredient I is many times higher in comparison with the racemate and not just twice as high, as expected. The activity can be 20 to 30 times higher, under certain conditions up to 100 times higher, than in the case of the racemate.

Conformation studies demonstrated that in the type of active ingredient in question of the acylalanines of the formula above, the right-hand side half of the molecule (see above) is fixed in a virtually vertical position relative to the 2,6-dimethylphenyl plane when in the crystalline state and that in solutions, when this barrier of rotation about the phenyl-N-axis can be overcome by energy, the methylene group to which the substituent R is attached forms an angle towards this phenyl group, as shown above by the formula (R. Nyfeler, P. Huxley, Monograph No. 31, British Crop Protection Conference Publication, Croydon 1985, p. 45 et seq.). This means that the remaining substituents in the molecule can vary their positions relative to the C atom of the alanine methyl ester, which is responsible for the absolute configuration. This also applies analogously to the compound furalaxyl, which has attached to it a 2-furanyl radical instead of the substituent CH₂-R, which is shown above.

In recent years, a plurality of biological investigations have confirmed, in principle, the finding that the R-enantiomer has a better fungicidal activity than the S-enantiomer. In Phytophthora palmivora, D.J. Fisher and A.L. Hayes (Crop protection [1985] $\underline{4}$ (4) pp. 501-510) found that the ED₅₀ inhibitory values in the nucleic acid synthesis were approximately fifty times more unfavorable in the case of the S-enantiomer of metalaxyl than in the case of the R-enantiomer, while the corresponding ED₅₀ values of R-enantiomer and racemate were in a ratio of approximately 3.1:5.6. The skilled man would thus expect that the activity of a given amount of R-enantiomer is approximately equivalent to twice the amount of racemate, and readily conclude that the much lower activity of the S-enantiomer in the racemate attributes, to this S-enantiomer, essentially the role of an inert material whose presence does not matter.

Resolution of the racemate of active ingredient I and use of the R-enantiomer only was therefore not an option for the practitioner, even if only because of the high level of action of the racemates, and has therefore not been proposed in the literature of the last 19 years as a solution for practical use.

Thus, it has to be assumed that, in the ready-for-use state of the racemic active ingredient I, the contribution of the R-enantiomer to the activity is reduced antagonistically by the

S-enantiomer and by other conformations of the molecule. For example, it would be conceivable that a large number of biochemical receptors are temporarily occupied by the ineffective components of the racemate I, but not permanently blocked. Since, furthermore, the active ingredients I, in particular metalaxyl and furalaxyl, became known for having a systemic and penetrating action, further negative effects of these isomers, which have previously prevented the rapid penetration capacity of the R-enantiomer into the cell tissue of the plant and have resulted in elevated losses due to volatilization, might also play a role.

The R-enantiomers of the formula I can be obtained for example by fractional crystallization of a salt prepared from N-(2,6-dimethylphenyl)- α -aminopropionic acid and an N-containing optically active base with subsequent liberation of the optically active antipode and esterification with methanol. An example of an optically active base is α -phenylethylamine (GB P.1 448 810).

Furthermore, the R-enantiomers of the active ingredients can also be obtained by the activation of the hydroxyl group as leaving group in the naturally occurring L(+) lactic acid, esters or salts, and its replacement by 2,6-dimethylaniline with reversal of configuration. The use of the acid or its salts necessitates subsequent esterification with methanol. The use of an lactic ester other than the methylester necessitates subsequent transesterification with methanol. The boiling point of pure R-metalaxyl is 143-145°C/0.03 mbar.

The active ingredient in question is formulated in a known manner to give pesticidal compositions, as is described, for example, in GB P.1 500 581.

The formulations are prepared in a known manner, for example by intimately mixing and/or grinding the active ingredients with extenders, such as, for example, with solvents, solid carriers and, if appropriate, surface-active compounds (surfactants).

Suitable carriers and additives can be solid or liquid and correspond to the substances expediently used in formulation technology, such as, for example, natural or regenerated mineral substances, solvents, dispersants, wetting agents, tackifiers, thickeners, binders or fertilizers.

A preferred method of applying the R-enantiomer is application to the aerial parts of the plant, especially the foliage (foliar application). Number and rate of application depend on

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the biological and climatic environmental conditions for the pathogen. Alternatively, the R-enantiomer can reach the plant via the soil through the root system (systemic action), by drenching the site of the plant with a liquid composition or by incorporating the substances into the soil in solid form, for example in the form of granules (soil application).

The compound is employed as pure active ingredient or, preferably, together with the adjuvants conventionally used in the art of formulation and is therefore processed in a known manner to give, for example, emulsion concentrates, spreadable pastes, directly sprayable or dilutable solutions, dilute emulsions, wettable powders, soluble powders, dusts, granules, or by encapsulation, for example in polymeric substances. The methods of application, such as spraying, atomizing, dusting, scattering, brushing on or pouring, as well as the type of the compositions, are selected to suit the intended aims and the prevailing circumstances.

As a rule, the agrochemical compositions comprise 0.1 to 99 %, in particular 0.1 to 95 %, of active ingredient I, 99.9 to 1 %, in particular 99.9 to 5 %, of a solid or liquid additive, and 0 to 25 %, in particular 0.1 to 25 %, of a surfactant.

While concentrated compositions are more preferred as commercially available goods, the end consumer uses, as a rule, dilute compositions. Such (agro)chemical compositions are part of the present invention.

The examples which follow are intended to illustrate the invention, "active ingredient I" preferably being metalaxyl, but also furalaxyl or benalaxyl, with a preferably high R-enantiomer content (70-100 % by weight).

Wettable powders	a)	b)	c)	d)
Active ingredient metalaxyl	25 %	50 %	75 %	24 %
(96 % R-enantiomer)			,	27 70
Sodium lignosulfonate	5 %	5 %	_	5 %
Sodium lauryl sulfate	3 %	-	5 %	4 %
Sodium diisobutylnaphthalene-	-	6%	10 %	-
sulfonate				
Octylphenol polyethylene glycol ether	_	2 %	-	_
(7-8 mol of ethylene oxide)				
Highly-disperse silica	<i>5</i> %	10 %	10 %	5 %
Kaolin	62 %	27 %	-	62 %

The active ingredient is mixed thoroughly with the additives and the mixture is ground thoroughly in a suitable mill. This gives wettable powders which can be diluted with water to give suspensions of any desired concentration.

Emulsion concentrate

Active ingredient metalaxyl	10 %
(96 % R-enantiomer)	
Octylphenol polyethylene glycol ether	3 %
(4-5 mol of ethylene oxide)	
Calcium dodecylbenzenesulfonate	3 %
Castor oil polyglycol ether	4 %
(35 mol of ethylene oxide)	
Cyclohexanone	30 %
Xylene mixture	50 %

Emulsions of any desired dilution, which can be employed in crop protection, can be prepared from this concentrate by diluting it with water.

Dusts	a)	b)	c)
Active ingredient I	5 %	6 %	4 %
(> 85 % R-enantiomer)			
Talc	95 %	-	-
Kaolin	•	94 %	-
Rock powder	-	-	96 %

Ready-for-use dusts are obtained by mixing the active ingredient with the carrier and grinding the mixture in a suitable mill.

Extruder granules

Active ingredient I	15 %
(> 92 % R-enantiomer)	
Sodium lignosulfonate	2 %
Carboxymethylcellulose	1 %
Kaolin	82.%

The active ingredient is mixed with the additives, and the mixture is ground and moistened

with water. This mixture is extruded and subsequently dried in a stream of air.

Coated granules

Active ingredient I	8 %
(> 70 % R-enantiomer)	
Polyethylene glycol (MW 200)	3 %
Kaolin	89 %
(MW = molecular weight)	

In a mixer, the finely ground active ingredient is applied uniformly to the kaolin which has been moistened with polyethylene glycol. In this manner, dust-free coated granules are obtained.

Suspension concentrate

Active ingredient I	40 %
(> 92 % R-enantiomer)	
Propylene glycol	10 %
Nonylphenol polyethylene glycol ether	6 %
(15 mol of ethylene oxide)	
Sodium lignosulfonate	10 %
Carboxymethylcellulose	1 %
Silicone oil	1 %
(in the form of a 75 % aqueous emulsion)	
Water	32 %

The finely ground active ingredient is mixed intimately with the additives. This gives a suspension concentrate from which suspensions of any desired dilution can be prepared by diluting it with water. Such dilutions can be used for treating live plants and plant propagation material by spraying, watering or immersing and for protecting them against attack by microorganisms.

I) Biological Examples

Test method

Vine plantlets cv. "Gutedel" are grown under greenhouse conditions using one plant per pot ($\emptyset = 6$ cm) and sprayed with a spray broth prepared from an emulsion concentrate, either in the two-leaf stage or in the three-leaf stage. The following concentrations of active ingredient are used per batch of 4 plants: 200; 60; 20; 6; 2; 0.6; 0.2; 0.06 mg of a.i./litre. This dilution series is prepared in demineralized water immediately prior to application as a foliar spray. To exclude a gas-phase effect of the a.i. in the vicinity, all plants are separated from each other on the side using translucent plastic foils and kept in the dark for one day at 20-22°C and a relative humidity of approximately 100 %.

Then, the entire leaf surface area of the plants is uniformly sprayed to drip point with a freshly prepared sporangia suspension (120 000/ml) of a metalaxyl-sensitive strain of *Plasmopara viticola*. The plants are then kept for 7 days under a 16 hour photoperiod with artificial daylight at 20-22°C and a relative humidity of approximately 100 %. This is followed by evaluation of the infestation, separating three-leaf and two-leaf stage sprayings. The tables show in each case the average of 4 parallel sprayings.

A) Sprayings in the two-leaf stage (Pl. viticola on vines)

Level of action of R-metalaxyl and racemic metalaxyl

Active	Dose	Foliar infestation [%]
ingredient	[mg of a.i./litre]	
	200	0
	60	0
	20	0
R-metalaxyl	6	0
	2	4
	0.6	78
	0.2	97
	0.06	92

untreated control		96	
	200	0	
	60	0	
	20	38	
racemic	6	76	
metalaxyl	2	87	
	0.6	100	
	0.2	97	
	0.06	96	

While conventional racemic metalaxyl does not result in a clear-cut action against foliar infestation in a concentration range of below 60 mg of a.i./litre and is without effect for practical purposes at a concentration of below 20 mg of a.i./litre, the activity of enantiomeric R-metalaxyl is up to 30 times better up to dilutions of 2 mg of a.i./litre.

In the case of spraying in the three-leaf stage, the differences in activity are even clearer, as shown by Table B).

B) Sprayings in the three-leaf stage (Pl. viticola on vines)

Level of action of R-metalaxyl and racemic metalaxyl

Active	Dose	Foliar infestation [%]
ingredient	[mg of a.i./litre]	
	200	0
	60	0
	20	0
R-metalaxyl	6	0 .
	2	0
	0.6	0
	0.2	78
	0.06	93
untreated control		92

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	200	0	
	60	0	•
	20	27	
racemic	6	85	
metalaxyl	2	80	
	0.6	96	
	0.2	90	
	0.06	92	

While conventional racemic metalaxyl shows virtually no activity in a concentration range of 6 mg of a.i./litre (or less) and a more clear-cut activity is only discernible at 20 mg of a.i./litre, the activity of enantiomeric R-metalaxyl is approximately 100 times better up to a concentration range of 0.6 mg of a.i./litre.

II) Degradation of the active ingredients in the soil

Example 1

Degradation behaviour of racemic metalaxyl and R-metalaxyl in moderately heavy soil

Two groups of 8 samples each of biologically active soil (silt/loam; loam: 13.9 %; silt: 54.3 %; sand: 31.8 %; organic carbon: 2.1 %; pH 7.3; biomass: 65.1 mg microbial carbon per 100 g soil; origin: Les Evouettes, Valais, Switzerland) are treated in parallel with racemic metalaxyl or R-metalaxyl, respectively, in each case in acetonic solution. The rate of application is 0.5 mg/kg of soil sample, which corresponds to a rate of application of 0.5 kg/hectare. The results are evaluated in duplicate after 0, 7, 14 and 21 days. Results:

Table 1: Rate of Degradation of rac. Metalaxyl and R-Metalaxyl in fieldfresh Soil (Silt/loam) under laboratory Conditions

Time (days)	racemic metalaxyl (% of applied)			R-metalaxyl (% of applied)	
		mean		mean	
0	90.41		93.61		
0	90.36	90.39	98.94	96.28	
7	47.28		24.74		
7	45.17	46.23	25.7	25.23	
14	35.88	1	9.07		
14	35.54	35.71	10.62	9.85	
21	29.34		7.57		
21	29.06	29.20	7.82	7.69	

The degradation equations are:

Metalaxyl racemate: $C_t = 86.66*_{e}(-0.0644*_{t})$

 $DT-50 = \ln 2/0.0644$; $DT-90 = \ln 10/0.0644$

R-metalaxyl: $C_t = 95.9*_{e}(-0.1776*t)$

 $DT-50 = \ln 2/0.01776$; $DT-90 = \ln 10/0.1776$

The degradation curves are shown in Figure 1 (Appendix).

They allow the following degradation times to be calculated:

	racemic metalaxyl	R-metalaxyl
DT-50:(50 % degradation)	10.8 days	3.9 days
DT-90:(90 % degradation)	35.7 days	13.0 days

Example 2

Degradation behaviour of racemic metalaxyl and R-metalaxyl in sandy soil

Two groups of 16 samples each of biologically active soil (sandy soil; loam: 5.1 %; silt: 11.4 %; sand: 83.5 %; organic carbon: 1.6 %; pH 4; biomass: 51 mg microbial carbon/100 g soil; origin: Collombey, Valais, Switzerland) are treated in parallel with racemic metalaxyl or R-metalaxyl, respectively, in each case in acetonic solution. The rate of application is 0.5 mg/kg of soil sample, which corresponds to a rate of application of 0.5 kg/hectare. The results are evaluated in duplicate after 0, 1, 3, 7, 9, 15, 21 and 29 days. Results:

Table 2: Rate of Degradation of rac. Metalaxyl and R-Metalaxyl in fieldfresh Soil (Sand) under laboratory Conditions.

racemic metalaxyl (% of applied)		R-metalaxyl (% of applied)	
	mean		mean
98.00		100.32	
97.56	97.78	99.72	100.02
87.75		89.16	
87.88	87.82	90.13	89.64
80.32		76.96	
79.69	80.01	74.01	75.48
65.41		52.59	
64.60	65.01	52.59	52.59
55.84		47.22	
56.68	56.26	46.45	46.84
43.49		24.77	
41.58	42.54		27.33
33.21	31.99	17.05	17.09
28.28	28.49	8.62	8.72
	98.00 97.56 87.75 87.88 80.32 79.69 65.41 64.60 55.84 56.68 43.49 41.58 30.77 33.21 28.70	(% of applied) mean 98.00 97.56 97.78 87.75 87.88 87.82 80.32 79.69 65.41 64.60 65.41 64.60 55.84 56.68 56.26 43.49 41.58 30.77 33.21 31.99	(% of applied) (% of applied) mean 100.32 97.56 97.78 99.72 87.75 89.16 87.88 87.82 90.13 80.32 76.96 79.69 80.01 74.01 65.41 52.59 55.84 47.22 56.68 56.26 46.45 43.49 41.58 42.54 30.77 17.12 33.21 31.99 17.05 28.70 8.82

Degradation equations

rac. Metalaxyl: Ct=93.67* e^(-0.05006*t); DT-50=ln 2/0.05006; DT-90=ln 10/0.5006 R-Metalaxyl: Ct=98.53* e^(-0.08548*t); DT-50=ln 2/0.08548; DT-90=ln 10/0.08548

The degradation curves are shown in Figure 2 (Appendix).

They allow the following degradation times to be calculated:

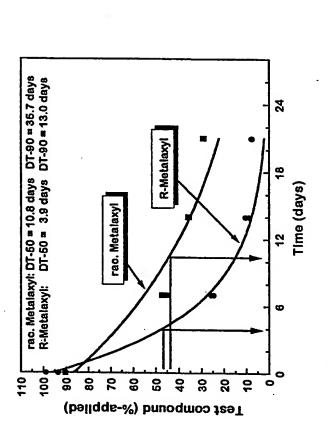
	racemic metalaxyl	R-metalaxyl
DT-50:(50 % degradation)	13.9 days	8.1 days
DT-90:(90 % degradation)	46.0 days	26.9 days

What we claim is:

- 1. A fungicidal composition having improved degradation in the soil, on the basis of an Oomycetes controlling fungicide selected from metalaxyl, furalaxyl and benalaxyl wherein the content of the R-enantiomer in the active ingredient is more than 70 % b.w., together with a suitable carrier material therefor.
- 2. A composition according to claim 1, wherein the content of the R-enantiomer in the active ingredient is more than 85 % by weight.
- 3. A composition according to claim 2, wherein the content of the R-enantiomer in the active ingredient is more than 92 % by weight.
- 4. A composition according to claim 3, wherein the content of the R-enantiomer in the active ingredient is more than 97 % by weight.
- 5. A composition according to claim 4, wherein the active ingredient is essentially free from S-enantiomer.
- 6. A composition according to claim 1, wherein the active ingredient enriched with R-enantiomer is metalaxyl.
- 7. A composition according to claim 1, wherein the active ingredient enriched with R-enantiomer is furalaxyl.
- 8. A composition according to claim 1, wherein the active ingredient enriched with R-enantiomer is benalaxyl.
- 9. A composition according to claim 6 comprising metalaxyl as highly concentrated formulation of more than 30 % b.w. active ingredient in addition to carrier material.
- 10. In a process for controlling or preventing attack of Oomycetes by applying to plants, parts of plants or to a locus liable to be infected by Oomycetes, a fungicide selected from metalaxyl, furalaxyl and benalaxyl the improvement that for better biodegradation in the soil the fungicide consists of more than 70 % b.w. of R-enantiomer.

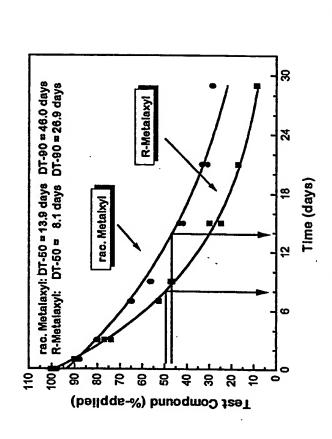
- 11. In a process according to claim 10 wherein the fungicide consists of more than 85 % b.w. of R-enantiomer.
- 12. In a process according to claim 11 wherein the fungicide used is metalaxyl consisting of more than 92 % b.w. of R-enantiomer.
- 13. In a process according to claim 12 wherein the metalaxyl used consists of more than 97 % b.w. of R-enantiomer.
- 14. In a process according to claim 11 wherein the fungicide used is benalaxyl consisting of more than 92 % b.w. of R-enantiomer.
- 15. In a process according to claim 11 wherein the fungicide used is furalaxyl consisting of more than 92 % b.w. of R-enantiomer.
- 16. In a process according to claim 10 wherein the rate of application corresponds to 60 g a.i. per hectare to 300 g a.i. per hectare of essentially pure R-enantiomer.

Figure 1: Rate of Degradation of rac. Metalaxyl and R-Metalaxyl in fieldfresh Soil (Siltloam) under laboratory Conditions.



DT-50: Disappearance Time for 50 % a.i.(Time until 50% of the fungicide are degraded) DT-90: Disappearance Time for 90 % a.i.(Time until 90% of the fungicide are degraded)

Figure 2: Rate of Degradation of rac. Metalaxyl and R-Metalaxyl in fieldfresh Soil (Sand) under laboratory Conditions.



DT-50: Disappearance Time for 50 % a.i. (Time until 50% of the fungicide are degraded) DT-90; Disappearance Time for 90 % a.i. (Time until 90% of the fungicide are degraded)

Interna 1 Application No PCT/EP 95/02544

A. CLASSIFICATION OF SUBJECT MATTER IPC 6 A01N37/46 A01N4: A01N43/08 According to International Patent Classification (IPC) or to both national classification and IPC B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 6 A01N Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practical, search terms used) C. DOCUMENTS CONSIDERED TO BE RELEVANT Citation of document, with indication, where appropriate, of the relevant passages Relevant to claim No. X GB, A, 1 448 810 (CIBA-GEIGY) 8 September 1-5,7, 1976 9-13,15 cited in the application see page 2, line 41 - page 3, line 23 see page 5, line 40 - line 46; claims 16 4,12,22,24; examples GB,A,1 500 581 (CIBA-GEIGY) 8 February X 1-6,9-13 1978 cited in the application see page 4, line 38 - page 5, line 43 see page 31, line 2 - page 32, line 33; claims 8,26-39 Y 16 Further documents are listed in the continuation of box C. X Patent family members are listed in annex. Special categories of cited documents: "T' later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the "A" document defining the general state of the art which is not considered to be of particular relevance invention 'E' earlier document but published on or after the international "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such docu-"O" document referring to an oral disclosure, use, exhibition or other means ments, such combination being obvious to a person skilled document published prior to the international filing date but later than the priority date claimed "&" document member of the same patent family Date of the actual completion of the international search Date of mailing of the international search report 27 October 1995 **15.** 11. 95 Name and mailing address of the ISA Authorized officer European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016 Fletcher, A

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